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(MVO's) WHICH ARE SUITED FOR CONFIGURATION INTERACTION CALCULATIONS

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ABSTRACT

A simple method, requiring the work of a single SCF iteration, is presented for the construction of Modified Virtual Orbitals (MVO's). Test calculations on H_2O, Ar and two states of CH_2 show that for the truncation of orbitals at the CI level, the MVO's are far more efficient than canonical SCF virtual orbitals or such related SCF virtuals as improved virtual orbitals (IVO's) and for some cases approach the efficiency of natural orbitals. MVO's are shown to be suitable for configuration selection based on energy contributions. The CI wavefunction is observed to be more compact with MVO's, allowing better interpretation of the results.

Introduction

Ideally one would like the CI expansion to be independent of the choice of orbitals; however, for all but the smallest problems this is impractical (for a general disucssion of CI, see ref. 1.). Over the last several years experience has lead to a few practical and reliable schemes for performing CI calculation: the all single and double excitations from all important reference configurations and the first order wavefunction (the POL-CI being essentially the same). However the size of the CI expansion grows so rapidly with the increase in problem size, that for large systems further approximations must be made. The most common approximations are the truncation of virtual orbitals or configuration selection based on energy contributions. Shavitt and co-workers[2] compared the efficiency of various one particle basis sets for orbital truncation and configuration selection based on energy contributions. They found that the orbitals could be grouped into two classes, natural orbitals (NO's), and SCF and related orbitals, where NO's were much more efficient than the SCF and SCF related orbitals. Unfortunately the additional work needed to compute the NO's (or pseudo NO's) outweigh the efficiency of a more compact CI expansion, and it is very common to truncate SCF virtual orbitals or select configurations based on energy contributions computed with SCF orbitals.

In addition to providing an efficient basis for orbital truncation and configuration selection based on energy contributions, the one particle basis should be chosen so that the wavefunction has a few impor-tant configurations accounting for a large percentage of the wavefunction. This compactness can be important in both reducing work and interpreting the results. For example, a compact wavefunction would minimize the

the number of reference configurations needed in all single and double excitation CI, thus reducing work while retaining accuracy. Also the appearance of an additional important configuration in the CI wavefunction indicates which additional terms should be added to the MCSCF and/or to the reference list, from which all single and double excitations are generated, in order to improve the wavefunction. The important configurations and the change in these configurations with geometry can also be useful in helping to understand the important correlation effects, thereby leading to better chemical understanding. CI wavefunctions computed with natural orbitals has this compactness, while wavefunctions computed from SCF orbitals do not. In general natural orbitals are not used to recompute the wavefunction because of the expense involved and one resorts to looking at the natural orbitals and the natural occupation numbers to gain a better understanding of the system.

In the light of the benefits of natural orbitals, it appears worthwhile to compare NO's with SCF and related orbitals. Davidson[3] has pointed out that the NO's with small occupation numbers (i.e., those corresponding to SCF virtual orbitals) lie in the same region of space as the occupied orbitals. The SCF virtual orbitals are much more diffuse, looking much more like an orbital that an additional electron would occupy. Hunt and Goddard[4] originally proposed Improved Virtual Orbitals (IVO's) for the computing of excited states, and since then these orbitals have been used for CI calculations. These orbtials look like excited state orbitals, and are therefore more contracted than SCF virtuals, but they are not as contracted as NO's. Tests[5] show that the IVO's are only slightly more efficient than SCF virtual orbitals in CI calculations. Davidson proposed Internally Consistent SCF orbitals (ICSCF orbitals)[6]. As with IVO's these orbitals are

produced with an n-1 potential. Shavitt[2] showed that the ICSCF orbitals are only slightly superior to SCF virtual orbitals.

While the IVO's and ICSCF orbitals represent an improvement over SCF virtual orbitals, they are by no means as effective as NO's. The reason is that the virtual orbitals are still too diffuse. In the MVO scheme, after the all electron SCF or MCSCF calculation is converged, all valence electrons are excluded and the Fock operator for the core electrons is constructed. This is transformed to a Fock matrix over molecular orbitals using the converged orbitals from the SCF or MCSCF. The subspace corresponding to the virtual orbitals in the all electron calculation is then diagonalized. These new virtual orbitals are called Modified Virtual Orbitals (MVO's). This procedure does not mix occupied and virtual orbitals. Since the core electrons are retained in the MVO step, the highest virtual orbitals should correspond to the core correlating functions (provided such functions are in the basis set). Without the valence electrons, the lowest virtuals should be drawn into the valence region and should be suitable for correlating the valence orbitals. It should be noted that this procedure is similar to IVO and ICSCF with the exception that the number of electrons removed is greater.

Rather than deleting electrons, an alternative technique would be to recompute the one electron integrals with an increased nuclear charge for all the nuclei. Then the all electron Fock operator could be constructed and the virtual subspace diagonalized. This process should be very similar to the elimination of valence electrons.

In the calculations reported here, all the valence electrons were removed in the MVO step; however, one can easily imagine a case where these MVO's might become too contracted. Consider the case of a Cu atom, where the 3s, 3p, 3d, and 4s electrons were to be correlated. If

all 19 electrons were deleted, the lowest d virtual orbital might
contain too much of the most contracted d basis function which was
added only to get the cusp correct. In this case, if fewer than 19
electrons were deleted the problem should be corrected. Thus with a
little experience one should be able to determine the optimum number
of electrons to be deleted for each case.

II. Test Calculations on CH_2, H_2O, and Ar

All calculations were performed using MOLECULE-Noname - SHI-CI[7].
The basis sets were all of double zeta plus polarization (DZP) quality.
For carbon, oxygen and hydrogen, we used Dunnings contraction[8] of the
Huzinaga primitive set[9], with oxygen and carbon (9s5p/4s2p) and
hydrogen (4s/2s) (with scale factor of 1.2). For Argon the primitive
set of Veillard[10] contracted (6111111/51111) yielding (12s9p/7s5p) was
used. A set of polarization functions was added to each atom: d's to
carbon, oxygen and argon and p's to hydrogen. The exponents were 0.75
(C), 1.0 (0), 1.0 (Ar) and 1.0 (H).

The geometry for H_2O was $\theta = 104.5°$ and $R(O-H) = 1.81$ a.u.,
for the $^1A_1$ state of CH_2, $\theta = 102.4°$ and $R(C-H) = 2.11$ a.u., and
for the $^3B_1$ state of CH_2, $\theta = 132.4°$ and $R(C-H) = 2.045$ a.u.

Single configuration SCF calculations were run for $H_2O(^1A_1)$,
$CH_2(^3B_1)$ and $Ar(^1S)$, while a two configuration MCSCF was run for
$CH_2(^1A_1)$. The configurations are:

$$\text{H}_2\text{O} \quad (^1A_1) \qquad 1a_1^2 \; 2a_1^2 \; 3a_1^2 \; 1b_1^2 \; 1b_2^2$$

$$\text{CH}_2 \quad (^3B_1) \qquad 1a_1^2 \; 2a_1^2 \; 3a_1^1 \; 1b_1^1 \; 1b_2^2$$

$$\text{Ar} \quad (^1S) \qquad 1s^2 \; 2s^2 \; 2p^6 \; 3s^2 \; 3p^6$$

$$\text{CH}_2 \quad (^1A_1) \qquad c_1 \; 1a_1^2 \; 2a_1^2 \; 3a_1^2 \; 1b_2^2 \; + \; c_2 \; 1a_1^2 \; 2a_1^2 \; 1b_1^2 \; 1b_2^2.$$

The CI expansions consisted of all single and double replacements from the reference configuration (or 2 reference configurations for $\text{CH}_2(^1A_1)$). In all calculations the core orbitals were frozen, thus the $1a_1$ orbital for CH_2 and H_2O and the 1s, 2s, and 2p orbitals for Ar were constrained to be fully occupied in all configurations. The orbitals used were the SCF orbitals, the MVO's and the natural orbitals as determined from the CI using the SCF orbitals. It was observed that the CI wavefunction is more compact when the MVO's or NO's are used. For $\text{CH}_2(^1A_1)$ the principle configurations are listed in Table 1. In the SCF orbital CI, the wavefunction is spread out over several terms; for example, two configurations which are important in the NO and MVO CI's are $1a_1^2 \; 2a_1^2 \; 3a_1^2 \; 1b_2^1 \; 2b_2^1$ and $1a_1^2 \; 2a_1^2 \; 3a_1^1 \; 2b_2^2$. These represent excitations, relative to the first reference configuration of $1b_2^1 \rightarrow 2b_2^1$ and $1b_2^2 \rightarrow 2b_2^2$, respectively. For the SCF orbital CI, it was found that $1b_2^2 \rightarrow 2b_2^2$, $1b_2^2 \rightarrow 2b_2^1 3b_2^1$, $1b_2^2 \rightarrow 3b_2^2$, $1b_2^2 \rightarrow 2b_2^1 4b_2^1$, $1b_2^2 \rightarrow 3b_2^1 4b_2^1$ and $1b_2^2 \rightarrow 4b_2^2$ are of approximately equal importance in describing b_2 to b_2 correlation.

When the natural orbitals were computed for the CI(SD) using MVO's, it was observed that the low lying MVO's are very similar to the low lying NO's, while the higher NO's represented linear combinations of higher MVO's.

III. Orbtial Truncation

Since the MVO's give a compact CI wavefunction, we tried deleting the highest virtual orbitals from the CI. We deleted 1, 3, 5, 7, 9, 11, 13, and 15 orbitals from H_2O and CH_2 and reran the CI(SD). This choice of orbitals is very arbitrary and on several occasions we were forced to choose between two orbitals with almost identical eigenvalue (MVO or SCF orbitals) or occupation number (NO's). In some cases the choice of which orbital to delete differed for SCF orbitals, MVO's or NO's. This actually makes the comparision more exaggerated than necessary, since in a practical calculation it is most likely that either both orbitals would be included or both excluded.

The calculations in Table II show the results for water. In this case the orbitals were deleted based on SCF virtual orbital eigenvalues. This simplified the calculation and the results for CH_2 show a maximum difference of 6 mh in total energy between, deleting all orbitals based on SCF eigenvalues and the case where NO's are deleted based on natural orbital occupation number, MVO's are deleted based on eigenvalue of the MVO's in the MVO step, and SCF orbitals are deleted on the basis of SCF eigenvalue. For water the orbitals tested were SCF, MVO and NO. Since the idea of MVO's is essentially to use virtual orbitals obtained from a highly positive ion, we also computed several positive ions and di-positive ions and used these virtual orbitals with the occupied orbitals from the SCF. We should note that the virtual orbitals taken from the positive ion should be very similar to the IVO's of Hunt and Goddard[4]. This allows a comparison with an alternative requiring as much work as MVO's. The results are very similar for all the different positive ions with the same charge and two representative ones are used in Table II.

Table III presents the comparison of orbital truncation for the two states of CH_2. In these calculations the orbitals were deleted separately for each calculation. The difference between NO's and MVO's is slightly bigger than with H_2O, but the MVO's still represent a large improvement over the SCF orbitals.

In all cases the MVO's are superior to SCF orbitals. The IVO's and virtuals coming from a di-positive ion are only a little better than the SCF orbitals and are far worse than the MVO's. It is clear that a fairly large charge is needed to contract the orbitals in order to make them suited for the correlation of the valence orbitals.

IV.   Energy Selection of Configurations

In these calculations we used a cumulative A_k selection procedure (for a description of this procedure, see ref. 11 and ref. 12). The results for Ar and CH_2 are summarized in Table IV. The first thing we should note is that the number of configurations with energy contribution greater than 0.001 is greater for MVO's than for NO's and the largest energy contributions are larger for MVO's. If normal selection procedures are followed for MVO's, we find the number of configurations is about the same as that for NO's, but the error is larger than that for SCF orbitals. If the threshold is reduced by 30 percent the number of configurations is about the same as that for SCF orbitals and the accuracy is about the same as for SCF orbitals. We noticed that for CH_2 ($^3B_1$) lowering the threshold by 30 percent still left the MVO selection error greater than that for the SCF orbitals. We investigated this and found two additional configurations with large energy contributions in the A_k (k=1) step. While these configurations were not so important that they need be added to the reference

list, they were important enough to be added to the k at the selection step. Thus the total number of unselected configurations remained unchanged, the selection was now based on three configurations. The added configurations were:

$$1a_1^2 \; 4a_1^2 \; 1b_2^2 \; 1b_1^1 \; 3a_1^1 \quad (2a_1^2 \rightarrow 4a_1^2 \text{, relative to the reference})$$

$$1a_1^2 \; 2a_1^2 \; 2b_2^2 \; 1b_1^1 \; 3a_1^1 \quad (1b_2^1 \rightarrow 2b_2) \text{ relative to the reference}).$$

We find that while the number of selected configurations remains the same, the error has been reduced.

It appears that a slightly different selection procedure is needed for MVO orbitals, requiring both a reduction of the cumulative threshold and increase in the k. Nevertheless, the same accuracy as with SCF or NO's can be obtained, while still retaining the compact wavefunction of MVO's.

V. Conclusion

A simple method was presented to compute Modified Virtual Orbitals. It was shown that the wavefunction is much more compact when MVO's are used, than with SCF virtual orbitals. This compactness is similar to that obtained by natural orbitals, but unlike natural orbitals, it requires little extra work. This compactness makes MVO's highly desirable for standard CI calculations where the compactness can lead to greater under-standing.

The MVO's are found to be much more effective than SCF orbitals for the deleting of orbitals at the CI level, but not as effective as natural orbitals.

The MVO's are shown to require a slightly different procedure for the selection of configurations based on energy contributions. The amount of work and accuracy is found to be about the same for MVO's and SCF orbitals (being somewhat more than NO's). The MVO's are probably still more desirable because of the compactness of the wavefunction.

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Table I. Principle configurations in the CI(SD) wave-
function for the $^1A_1$ state of CH_2. Listed
are those configurations with a coefficient
greater than 0.05 in any of the CI wavefunctions.
Configurations 1 and 2 are the reference con-
figurations.

	ORBITALS		
Configuration	SCF	MVO	NO
$1a_1^2\ 2a_1^2\ 3a_1^2\ 1b_2^2$	0.9584	0.9584	0.9574
$1a_1^2\ 2a_1^2\ 1b_2^2\ 1b_1^2$	-0.1868	-0.1868	-0.1923
$1a_1^2\ 2a_1^2\ 3a_1^2\ 2b_2^2$	-0.0266	-0.0614	-0.0618
$1a_1^2\ 2a_1^2\ 3a_1^2\ 1b_2^1\ 2b_2^1$	0.0272	0.0662	-0.0569
$1a_1^2\ 3a_1^2\ 4a_1^2\ 1b_2^2$	-0.0240	-0.0564	-0.0450

Table II. CI energies for $^1A_1$ state of H_2O as a function of number of deleted orbitals.

		TYPE OF ORBITALS			
	Occupied SCF	SCF	SCF	SCF	NO
	virtual SCF	H_2O^+ $^2A_1$	H_2O^{++} a	MVO	NO
N 0	-76.246649	-76.246649	-76.246649	-76.246649	-76.246649
u 1	-76.246564	-76.246564	-76.246565	-76.246624	-76.246367
m 3	-76.232993	-76.233826	-76.235112	-76.244063	-76.246006
b 5	-76.219759	-76.221539	-76.224091	-76.241001	-76.243613
e 7	-76.203449	-76.206189	-76.210073	-76.236529	-76.239548
r 9	-76.186126	-76.189373	-76.193892	-76.229874	-76.235599
11	-76.174051	-76.176828	-76.180652	-76.209471	-76.215215
13	-76.158282	-76.160395	-76.163246	-76.190544	-76.194501
15	-76.122671	-76.129099	-76.138155	-76.176354	-76.179828

Number of deleted orbitals

a configuration $1a_1^2\, 2a_1^2\, 1b_1^2\, 1b_2^2$

Table III. The effects of orbital truncation on the CI energy of CH$_2$ for various choices of orbitals.

Number of orbitals deleted	$^1A_1$			$^3B_1$		
Orbitals	SCF	MVO	NO	SCF	MVO	NO
0	-39.020142	-39.020142	-39.020053	-39.041485	-39.041485	-39.041459
1	-39.020112	-39.020115	-39.020034			
3	-39.015644	-39.017811	-39.019584	-39.037848	-39.039888	-39.040852
5	-39.010965	-39.014716	-39.017947	-39.033450	-39.037177	-39.039345
7	-39.007843	-39.011423	-39.014827	-39.028726	-39.033471	-39.036676
9	-38.997528	-39.004093	-39.011232	-39.020605	-39.027179	-39.033043
11	-38.984538	-38.998986	-39.007464	-39.005704	-39.020949	-39.026754
13	-38.968769	-38.987121	-39.000156	-38.991503	-39.010915	-39.013682
15	-38.947697	-38.973546	-38.984204	-38.970083	-38.995751	-38.998356

Table IV. Comparison of energy selection of configurations

Molecule	k	Orbitals	Full	CSF's	Threshold	Selected	CSF's	Error
Ar (^{1}S)	1	SCF	-526.937609	477	1.0 mh	-526.936369	226	1.2 mh
	1	MVO	-526.937609	477	1.0 mh	-526.936203	212	1.4 mh
	1	MVO	-526.937609	477	0.7 mh	-526.936464	226	1.1 mh
	1	NO	-526.937424	477	1.0 mh	-526.936696	215	0.7 mh
CH$_2$ (^{1}A$_1$)	2	SCF	-39.020142	1232	1.0 mh	-39.018513	568	1.6 mh
	2	MVO	-39.020142	1232	1.0 mh	-39.108238	514	1.9 mh
	2	MVO	-39.020142	1232	0.7 mh	-39.108662	561	1.4 mh
	2	NO	-39.020053	1232	1.0 mh	-39.108724	554	1.3 mh
CH$_2$ (^{3}B$_1$)	1	SCF	-39.041485	1836	1.0 mh	-39.039967	820	1.5 mh
	1	MVO	-39.041485	1836	1.0 mh	-39.039557	739	1.9 mh
	1	MVO	-39.041485	1836	0.7 mh	-39.039880	797	1.6 mh
	1	NO	-39.041459	1836	1.0 mh	-39.039963	717	1.5 mh
	3	MVO	-39.041485	1836	1.0 mh	-39.039767	737	1.7 mh
	3	MVO	-39.041485	1836	0.7 mh	-39.040068	796	1.4 mh